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**The Interaction of the Polyimide Precursors PMDA and m-PDA with Ni(110)**

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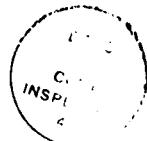
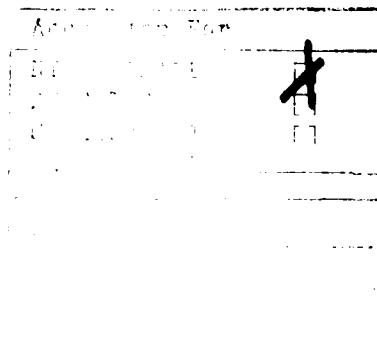
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(revised 23 August 1989)

**Abstract**

X-ray photoelectron spectroscopy (XPS) and high resolution electron energy loss spectroscopy (HREELS) have been used to study the adsorption of polyimide precursor molecules on Ni(110) and their subsequent reaction to form polyimide. PMDA (1,2,4,5-benzenetetracarboxylic anhydride) and m-PDA (1,3-phenylenediamine) were vapour deposited *in vacuo* at substrate temperatures of between 150 and 300K. Both m-PDA and PMDA adsorb at 300K without major fragmentation. For m-PDA, adsorption to the surface occurs via its nitrogen atoms. HREELS results suggest that significant deprotonation of the amine groups occurs and that the plane of the aromatic ring is inclined away from the surface normal. For PMDA, XPS results indicate that the primary chemical interaction with the Ni is through at least one of the anhydride oxygens. HREELS results imply that the plane of the aromatic ring is aligned close to the surface normal, therefore it is concluded that adhesion to the surface is through one anhydride unit only.



A-1

## 1. Introduction

Polyimide is a type of polymer which is widely used as an interlevel dielectric in microelectronic packaging. In this application it is essential to have reliable adhesion between the polyimide and other materials. This need has provided motivation for a large number of studies of the chemical and physical properties of the polyimide-metal interface [1-5]. One method to form a polyimide film is to co-deposit the dianhydride and diamine precursor molecules directly onto the substrate, where they react to form polyamic acid which is converted into polyimide by heating [6]. It is of considerable interest therefore to understand the chemical interactions of the precursor molecules with various materials.

The majority of studies of the polyimide-metal interface have concentrated on the polyimide PMDA-ODA, where PMDA is pyromellitic dianhydride (1,2,4,5-benzenetetracarboxylic anhydride) (Fig. 1(a)) and ODA is 4,4'-oxydianiline, (Fig. 1(b)) [1-5,7-9]. Adsorption of both PMDA and ODA has been studied on Cu and Ag substrates using x-ray photoelectron spectroscopy [7-9]. The PMDA molecule interacts through one end with the loss of carbon and oxygen; its molecular axis is tilted up from the surface exposing the intact end of the molecule for reaction with ODA, thus providing a strong anchor to the surface. The interaction of the ODA molecule is complex and poorly understood. Partial fragmentation occurs with the possible loss of aniline and oxidation of the metal surface.

In this paper, we describe the adsorption of meta-phenylene diamine (1,3-diaminobenzene or m-PDA) (Fig. 1(c)) and PMDA onto a Ni(110) surface. The bonding and orientation of the adsorbed molecules were characterized with x-ray photoelectron spectroscopy (XPS) and high resolution electron energy loss spectroscopy (HREELS). The m-PDA molecule is simpler than ODA, as seen in Fig. 1. In particular, the absence of oxygen simplifies interpretation of the XPS and HREELS spectra. Preliminary HREELS results have been reported previously [10].

## 2. Experimental

Two Ni(110) crystals were used for this work, both cut from the same boule. Both crystals were mechanically polished and then cleaned in ultra-high vacuum using standard argon ion sputtering and annealing (900-1000K) procedures.

Measurements at the University of Liverpool were made in a UHV chamber (base pressure  $< 2 \times 10^{-10}$  mbar) equipped with HREELS (VSW Scientific Instruments Ltd.), Auger electron spectroscopy (AES) and mass spectroscopy. The HREEL spectrometer consists of a fixed monochromator and rotatable analyser, both of the hemispherical deflector type, fitted with four element lenses [11]. Surface cleanliness was monitored using AES and HREELS. Both the PMDA (Lancaster Synthesis Ltd., 97% purity) and m-PDA (Lancaster Synthesis Ltd., 98% purity) samples were deposited from a side chamber, which was independently pumped (base pressure  $\sim 2 \times 10^{-7}$  mbar) and could be isolated by a gate valve from the main chamber. Both samples were contained in a ceramic dish and heated using an external heating tape whilst being pumped (pressures in the dosing line typically rose to  $2 \times 10^{-4}$  mbar upon heating). Temperatures were monitored using a chromel-alumel thermocouple wire and source temperatures were kept at approximately 40°C for m-PDA and 75°C for PMDA. Both samples were loaded as quickly as possible into the dosing chamber to minimise exposure to moisture in the air. This is particularly important for PMDA which hydrolyses easily in air. The samples were continuously heated and pumped for several hours before opening the valve to the

main chamber for dosing. Typical dosing pressures in the main chamber were  $2 \times 10^{-7}$  mbar for PMDA and  $2 \times 10^{-6}$  mbar for m-PDA. HREEL spectra were recorded in both specular and off-specular scattering geometries, with a resolution of about 8-10 meV ( $64-80 \text{ cm}^{-1}$ ) full-width half maximum (FWHM) in the elastic peak in specular scattering geometry.

The XPS measurements were performed at the University of Maine using a hemispherical analyzer (VSW Scientific Instruments, Ltd., model HA5000) operated in the constant resolution mode with a pass energy of 25 eV. The energy resolution in this mode was about 1.6 eV FWHM. The binding energy scale was calibrated using the spectrum of clean Cu. Both Al and Mg x-ray anodes were used. The analysis chamber (base pressure  $\sim 6 \times 10^{-10}$  mbar) also contains an HREELS spectrometer [12] which was operated at a resolution of about 15 meV FWHM, in specular scattering geometry. Surface cleanliness was monitored using XPS.

The PMDA (Aldrich, zone-refined, > 99% purity) and m-PDA (Aldrich, zone-refined, 99% purity) samples were deposited from separate sources consisting of copper tubes with 0.2 mm diameter apertures ; and holding approximately 1 cm<sup>3</sup> of powdered sample. Each tube is mounted in a MACOR holder wrapped with Ta wire, which is used for resistive heating of the source. The source temperature is measured with a chromel-alumel thermocouple which passes through a small hole drilled in the holder. Source temperatures were again kept near 75°C for PMDA and 40°C for m-PDA. The sources are mounted in a separately pumped side chamber which can be isolated from the main vacuum chamber by a gate valve. At the start of a deposition, the sources are translated into the main vacuum chamber and positioned directly in front of the substrate. Upon completion of the deposition, the sources are withdrawn and the gate valve closed. This procedure is essential for rapid recovery of good vacuum conditions since it minimizes the amount of PMDA and m-PDA deposited on the main chamber walls. Typical pressures in the main chamber during deposition were  $5 \times 10^{-6}$  mbar for m-PDA and  $4 \times 10^{-7}$  mbar for PMDA.

The thickness  $d$  of the adsorbed layers was estimated from the attenuation of the Ni 2p<sub>3/2</sub> and Ni 3p emission using the expression

$$I(E) = I_0(E) e^{-d/\lambda_E} \quad (1)$$

where  $I_0(E)$  is the intensity from the clean surface,  $I(E)$  is the intensity after deposition, and  $\lambda_E$  is the value of the electron mean-free pathlength in the adsorbate at kinetic energy  $E$ . For Al K<sub>α</sub> x-rays,  $E$  is 635 eV for Ni 2p<sub>3/2</sub> photoelectrons and 1422 eV for Ni 3p photoelectrons. The  $E$ -dependence of  $\lambda_E$  is often assumed to be of the form [13]

$$\lambda_E \propto E^m \quad (2)$$

where  $m$  typically lies in the range  $0.5 < m < 0.7$  [9]. Eqn. 1 assumes that the adsorbate layer is uniform and homogeneous. In this case, Eqns (1) and (2) can be used to extract  $m$  from the data. We find  $m = 0.4$  for m-PDA and  $m = 0.86$  for PMDA. The magnitude of  $\lambda_E$  is not accurately known; we have used  $\lambda_{635} = 10 \text{ \AA}$  and calculated other values using Eqn (2). This is consistent with previous studies of PMDA and ODA [7-9].

The average composition of the m-PDA and PMDA layers was estimated from the relative integrated intensities of the XPS signals using [9]

$$N_1/N_2 = (I_1/I_2) (\sigma_2/\sigma_1) (E_2/E_1)^{m-T} \quad (3)$$

for thick films ( $d \gg \lambda_E$ ) and

$$N_1/N_2 = (I_1/I_2)(\sigma_2/\sigma_1)(E_2/E_1)^{-T} \quad (4)$$

for thin layers ( $d \ll \lambda_E$ ) where  $\sigma$  is the relative photoelectron cross section [14] and  $T$  describes the energy dependence of the spectrometer transmission function.  $T$  was measured to be  $1.6 \pm 0.2$  using the procedure described by Seah and Anthony [15].

### 3. Results

#### 3.1. m-PDA

The Ni surface was cooled to about 220 K and exposed to m-PDA for 20 min at a background pressure of  $5 \times 10^{-6}$  mbar. The condensed m-PDA layer was thick enough to completely attenuate the Ni  $2p_{3/2}$  emission and to reduce the Ni emission at the Fermi level by more than 99%. Figure 2(a) and 2(b) show the C 1s and N 1s spectra obtained from such a layer. The N 1s spectrum, Fig. 2(b), consists of a single line at 400.0 eV binding energy with FWHM equal to the instrumental resolution. There is also a weak shake-up satellite at about 406.5 eV. The C 1s line, Fig. 2(a), consists of an unresolved doublet and a shake-up at 291.0 eV. The more intense, low binding energy component of the doublet is at 285.1 eV and is assigned to carbon atoms which are not bonded to nitrogen. The other component at 286.5 eV is assigned to carbon atoms which are bonded to nitrogen. These components have the two-to-one intensity ratio expected from the structure of the m-PDA molecule. There is no evidence for charging shifts for the condensed m-PDA film.

The HREELS spectrum for a condensed layer is shown in Fig 3(a). Loss energies are in strong agreement with infra-red absorption spectra recorded for the bulk sample and a more complete assignment will be presented elsewhere [16]. In this paper, we concentrate on the C-H and N-H stretching modes observed near 400 meV. Peaks at 405 meV ( $3266 \text{ cm}^{-1}$ ) and 427 meV ( $3444 \text{ cm}^{-1}$ ) are assigned to the symmetric and anti-symmetric modes within the  $\text{NH}_2$  groups based on comparison with infra-red absorption. The integrated intensity of the N-H loss peaks is comparable to that in the C-H loss at 376 meV ( $3032 \text{ cm}^{-1}$ ).

Exposure to m-PDA was also carried out with the Ni crystal at 300 K. At saturation coverage, the thickness of the adsorbed layer was found to be  $d = 1.04 \lambda_{635}$  and  $d = 0.76 \lambda_{1422}$  respectively, corresponding to a thickness of about 10 Å. The lower curves in Fig. 2(a) and 2(b) show the C 1s and N 1s spectra respectively. The changes in the C 1s lineshape are small; the doublet is not as apparent and there is a tail to higher binding energies which nearly obscures the shake-up feature. In contrast, the N 1s line is changed significantly; the maximum has shifted about 1.3 eV to lower binding energy and the FWHM has doubled. Clearly, nitrogen is now present in at least two chemical states; the adsorption induced state at lower binding energy (398.7 eV) contains more than 40% of the nitrogen atoms, based on fits using two gaussians. Nitrogen is not lost from the surface since the nitrogen-to-carbon ratio, calculated using Eqn 4, is the same as for the thick, condensed layer.

Specular and non-specular HREEL spectra for m-PDA adsorbed at 300 K are shown in Fig. 3(c) and (b) respectively. The N-H stretching modes at 405 meV and 427 meV are very weak compared to condensed m-PDA, Fig 3(a). This implies a significant

dehydrogenation of the amine groups. The observation of the out-of-plane C-H bending mode at 95 meV ( $766\text{cm}^{-1}$ ), preferentially in specular geometry (Fig. 3(c)) indicates that this mode is strongly surface dipole active [17] and thus the dynamic dipole, which is perpendicular to the aromatic ring, has a large component along the surface normal. The plane of the aromatic ring, therefore, must be far from perpendicular to the surface.

### 3.2. PMDA

A thick layer of PMDA was condensed onto the Ni(110) sample at 140 K. The layer was thick enough to completely attenuate both the Ni  $2p_{3/2}$  and the Ni 3p emission and the emission near the Fermi level was attenuated by 98%. The C 1s and N 1s spectra are shown in Fig. 4(a) and 4(b) respectively and are in good agreement with previous studies [7,8]. The spectra have been shifted by 1.3 eV to lower binding energies for direct comparison with the C 1s emission from a thin PMDA film. This magnitude "charging" shift is typical for thick layers of PMDA [8]. The C 1s peak at 283.2 eV is due to carbon atoms in the phenyl ring and the peak at 287.0 eV is due to carbonyl carbon atoms. The carbonyl emission tails off on the high binding energy side with a small shake-up feature at about 289.2 eV. The O 1s peak is an unresolved doublet with a shake-up feature at about 536.5 eV; the low binding energy component is due to carbonyl oxygen atoms.

Figure 4 also shows data for a thin layer of PMDA deposited at 300 K. Attenuation of the Ni  $2p_{3/2}$  and the Ni 3p signals yield thicknesses of  $0.22\lambda_{635}$  and  $0.11\lambda_{1422}$  respectively, or about 2-3 Å. If the deposit is assumed to have uniform thickness, these results imply that the mean-free pathlength at 1422 eV kinetic energy is twice as long as at 635 eV. This ratio is only 1.4 for the m-PDA layer deposited at 300 K. Since  $\lambda$  increases at larger kinetic energies [13], this difference implies that the m-PDA layer is much less uniform than the PMDA deposit.

Although, the carbonyl component of the C 1s line, Fig. 4(a), is reduced in intensity and slightly broadened relative to condensed PMDA, its integrated intensity still accounts for about 0.4 of the total C 1s intensity. The O 1s emission has more significant changes. The shake-up feature has nearly disappeared and the shoulder on the high binding energy side is less pronounced. This change in the shoulder could be caused by a shift of at least one of the anhydride oxygens to lower binding energy. As is the case for m-PDA, the stoichiometry of the PMDA layer formed at 300 K is the same as condensed PMDA. The O 1s line for oxidized Ni(110) has a binding energy of about 529 eV. If any oxide was formed, a new shoulder would be expected to form further on the low binding energy side of the O 1s line.

Specular and off-specular HREEL spectra for PMDA adsorbed on Ni(110) at 300K are shown in Fig. 5. Similar loss features were observed in both scattering geometries although some changes in the relative intensities of loss features can be distinguished. In particular, the feature at 156 meV ( $1258\text{ cm}^{-1}$ ) shows a clear loss in relative intensity away from specular as does the feature at 226 meV ( $1823\text{ cm}^{-1}$ ). The size and complexity of the PMDA molecule makes it difficult to assign all the loss features unambiguously. A more detailed analysis will be presented elsewhere [16] but, for the purposes of this paper, the salient features are the losses at 362 meV ( $2920\text{ cm}^{-1}$ ) and 379 meV ( $3057\text{ cm}^{-1}$ ), assigned to C-H stretching vibrations, the loss at 226 meV ( $1823\text{ cm}^{-1}$ ) assigned to C=O stretching vibrations of the carbonyl groups and the strongly specular mode at 156 meV ( $1258\text{ cm}^{-1}$ ) which we assign to the symmetric C-O stretch of the C-O-C grouping in the anhydride units. On the basis of its frequency, the latter feature could be associated with an in-plane C-H bending mode (typically  $1250\text{-}1310\text{ cm}^{-1}$ ) for a 1,2,4,5-substituted benzene

[18], but this is dipole inactive in the free PMDA, as with an in-plane ring deformation mode (typically 1220-1280  $\text{cm}^{-1}$ ) though this has only very weak dipole activity in the free molecule. The symmetric (and also asymmetric) C-O-C stretch is, however, strongly dipole active. The observation of two C-H stretching vibrations is a clear indication that the two hydrogen atoms in the molecule are in significantly different environments in the adsorbed species. The low frequency of one of these modes (2920  $\text{cm}^{-1}$ ) suggests that it is located rather close to the metal surface which is known to soften C-H stretching modes [19]. The observation of carbonyl stretching modes argues that at least one of the anhydride units remains intact. One expects in-phase and out-of-phase CO vibrations for anhydride units and in the closely related phthalic anhydride ( $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ ) these are located at 1865  $\text{cm}^{-1}$  and 1802  $\text{cm}^{-1}$  respectively. Our observation of a band at 1823  $\text{cm}^{-1}$  with FWHM of *ca.* 150  $\text{cm}^{-1}$ , i.e. twice that of the elastic peak, suggests both features are present in the observed band. The marked surface dipole activity of the symmetric C-O-C stretching vibration clearly indicates that the dynamic dipole associated with this mode must have a large component perpendicular to the Ni surface. The plane of the molecule must be highly inclined away from the surface.

The loss feature at 111 meV (895  $\text{cm}^{-1}$ ), which appears not to show a strong dipole activity could be assigned to the asymmetric C-O-C anhydride stretch (904  $\text{cm}^{-1}$  in phthalic anhydride) or the in-phase C-H, out-of-plane bending mode (860-910  $\text{cm}^{-1}$  in 1,2,4,5 substituted benzenes [18]). The latter of these, which is usually a strong feature of aromatic systems (see Fig. 3(c) for m-PDA), becomes dipole inactive if the aromatic ring is perpendicular to the surface.

In summary, the HREELS data points to a molecule which is not strongly perturbed or fragmented by adsorption on Ni(110) at room temperature. Together with the XPS data, the indications are that the molecular plane is highly inclined relative to the Ni surface, bonding is through only one anhydride unit and the plane of the molecule is such that the C-H bands are inequivalent with one H atom close to the surface.

#### **4. Conclusions**

We have studied the adsorption of the polyimide precursor molecules m-PDA and PMDA onto a clean Ni(110) surface.

For adsorption at 300 K, m-PDA bonds to the nickel substrate via its nitrogen atoms and does not undergo major fragmentation. The very weak N-H stretching mode is indicative of dehydrogenation and the formation of a strong low binding energy N 1s state shows that at least one-half of the nitrogen atoms are involved in the bonding. The observation of the relatively strong out-of-plane C-H bending mode, in specular HREELS, also provides evidence that the plane of the aromatic ring is inclined away from the surface normal. This orientation would provide a steric barrier for subsequent bonding to PMDA.

The aromatic ring is inclined towards the surface normal probably leaving a free anhydride unit available for subsequent reaction with m-PDA to form polyimide. The broadening of the carbonyl component of the C 1s emission demonstrates that the carbonyl bonding is also slightly altered but that the carbonyl groups remain intact. This implies weaker bonding than observed for PMDA on Cu and Au where C and O are lost.

These results imply that PMDA to m-PDA polyimide films grown on Ni(110) by vapor deposition will be chemically bonded to the surface only through the PMDA and that adhesion will be weak compared to films grown on copper or silver substrates.

### **Acknowledgements**

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**FIGURE CAPTIONS**

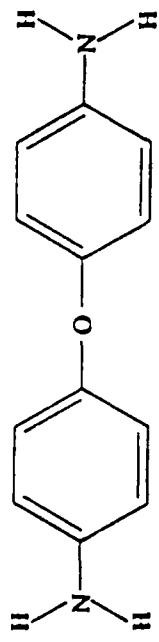
Figure 1. Structural units of: (a) Pyromellitic dianhydride (PMDA or 1,2,4,5-benzenetetracarboxylic anhydride); (b) 4,4'-oxydianiline (ODA); (c) meta-phenylenediamine (m-PDA or 1,3-diaminobenzene); (d) structural unit of PMDA - m-PDA polyimide.

Figure 2. XPS spectra for a thick layer of m-PDA adsorbed on Ni(110) at 220 K (crosses) and 300 K (squares): (a) C 1s; (b) N 1s. The spectra have been multiplied by the indicated scale factors.

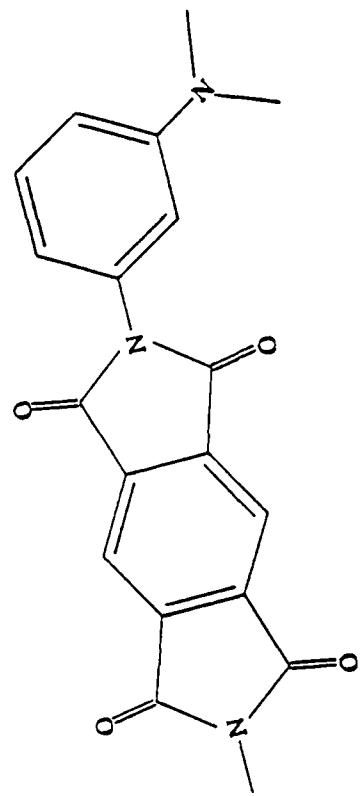
Figure 3. HREEL spectra for m-PDA adsorbed on Ni(110). Spectrum (a): A thick film condensed at 150 K. Spectra (b) and (c): saturation coverage at 300 K. The incident energy was 4 eV. Spectra (a) and (c) were recorded in specular scattering geometry ( $\theta_i = 60^\circ$ ,  $\theta_s = 60^\circ$ ) and spectrum (b) is 20° off-specular ( $\theta_i = 60^\circ$ ,  $\theta_s = 40^\circ$ ).

Figure 4. XPS spectra for a thick layer of PMDA adsorbed on Ni(110) at 140 K (crosses) and 300 K (squares): (a) C 1s; (b) O 1s. The spectra have been multiplied by the indicated scale factors.

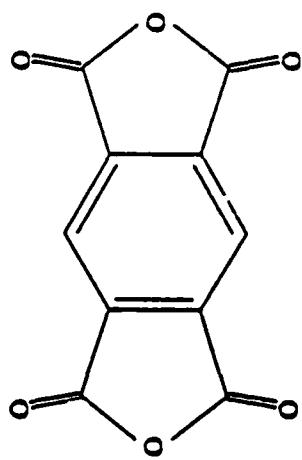
Figure 5. A specular HREEL spectrum for PMDA adsorbed on Ni(110) at 300 K. The incident electron energy was 10 eV: (a) 20° off-specular ( $\theta_i = 60^\circ$ ,  $\theta_s = 60^\circ$ ) and (b) specular scattering geometry ( $\theta_i = 60^\circ$ ,  $\theta_s = 40^\circ$ ).



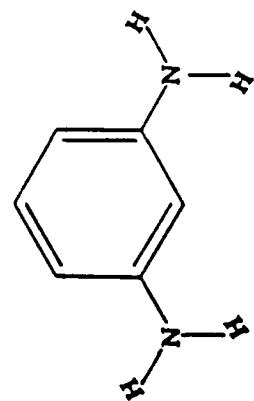
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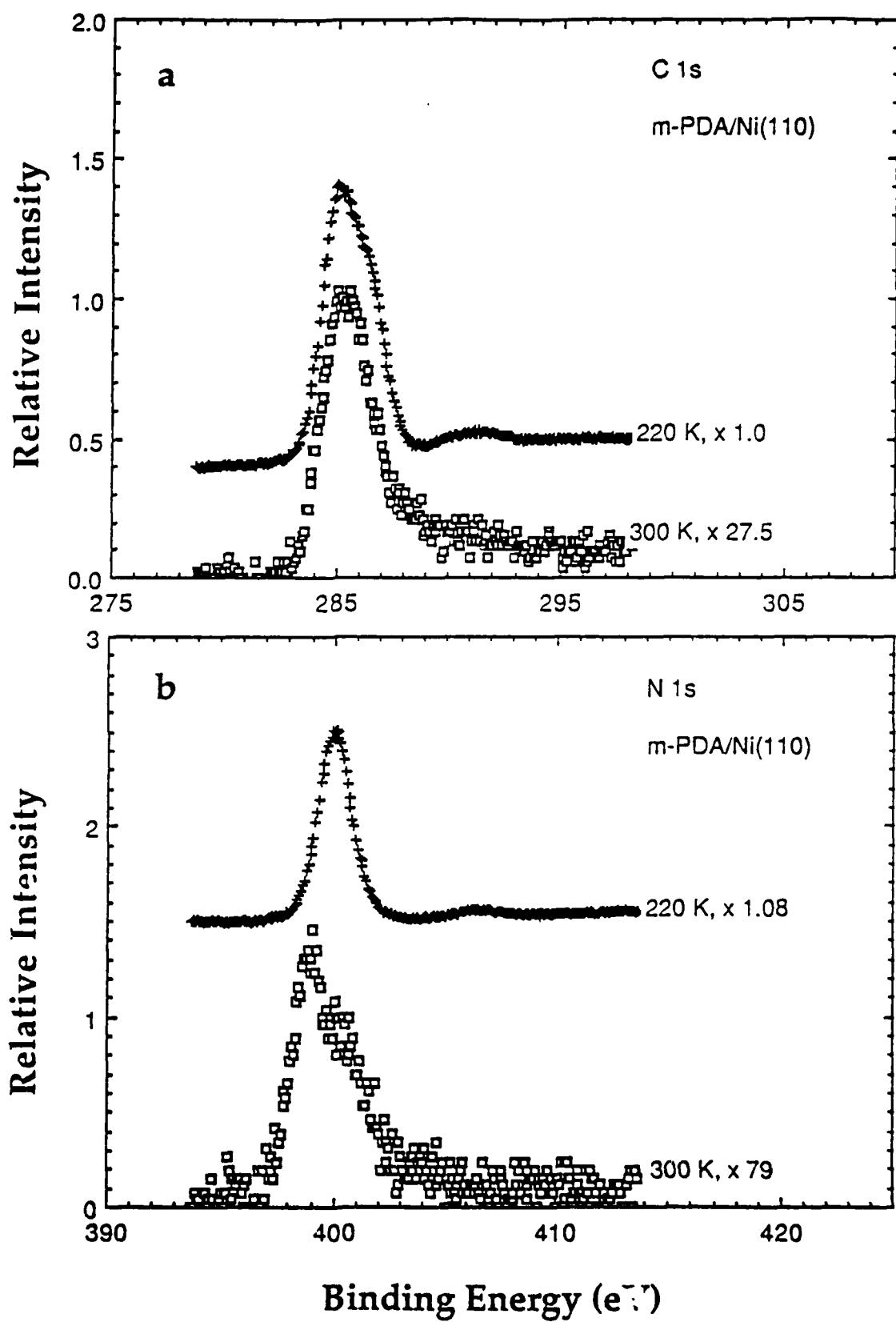
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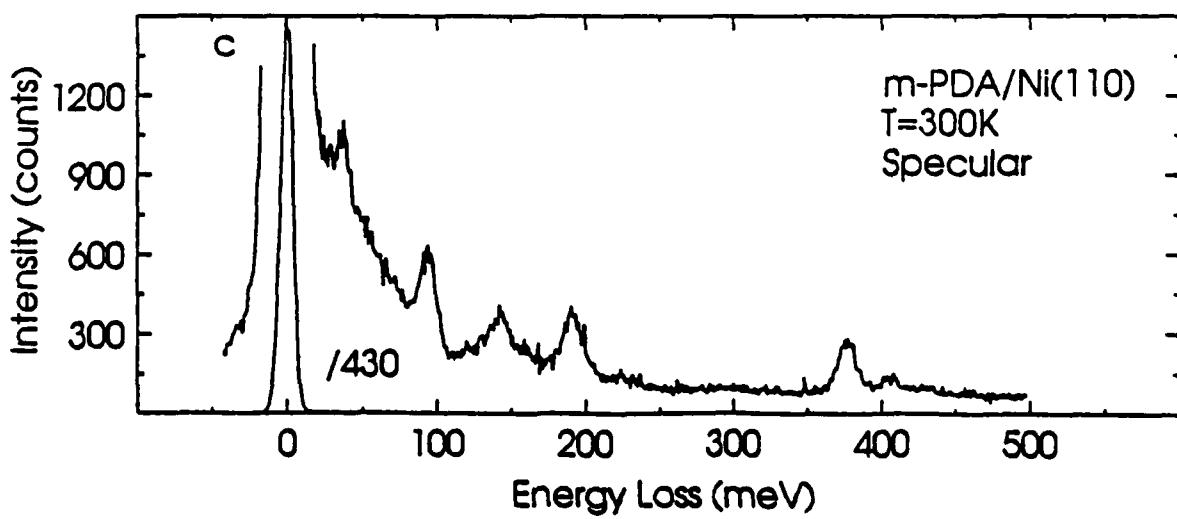
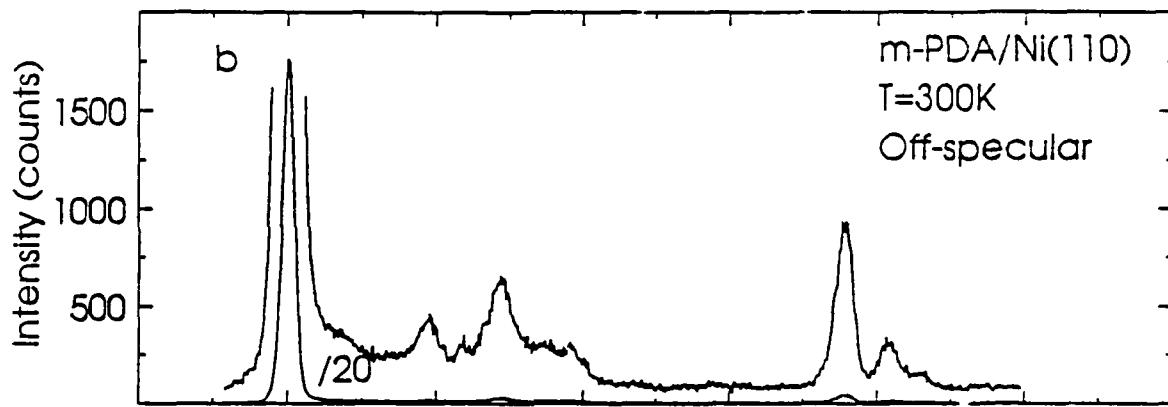
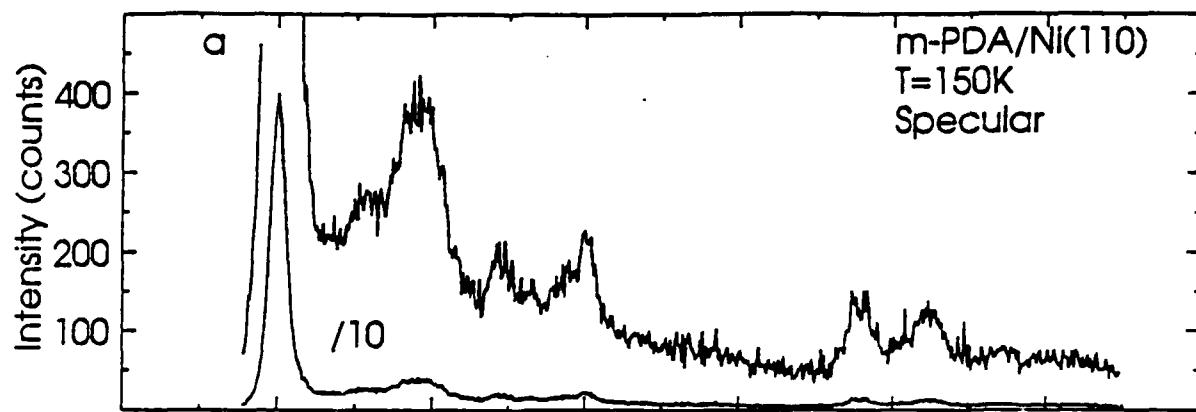


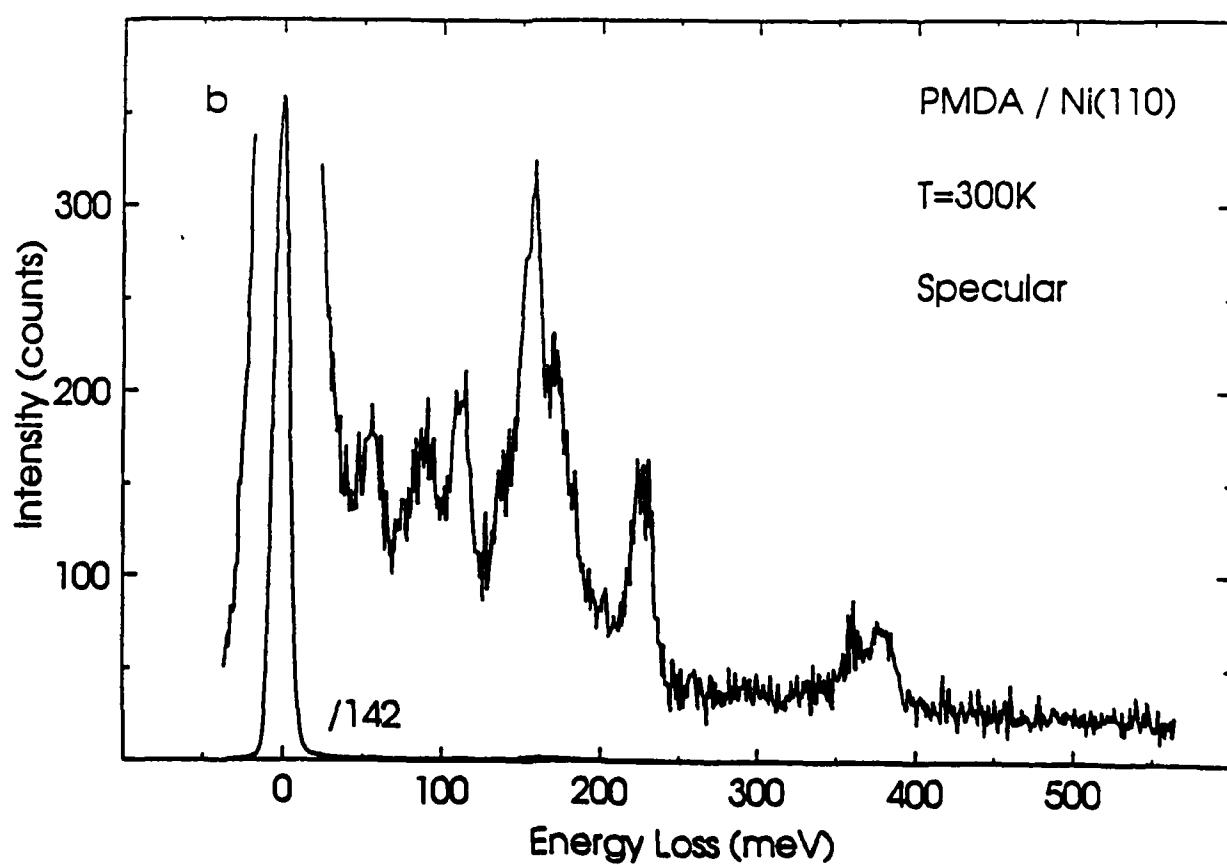
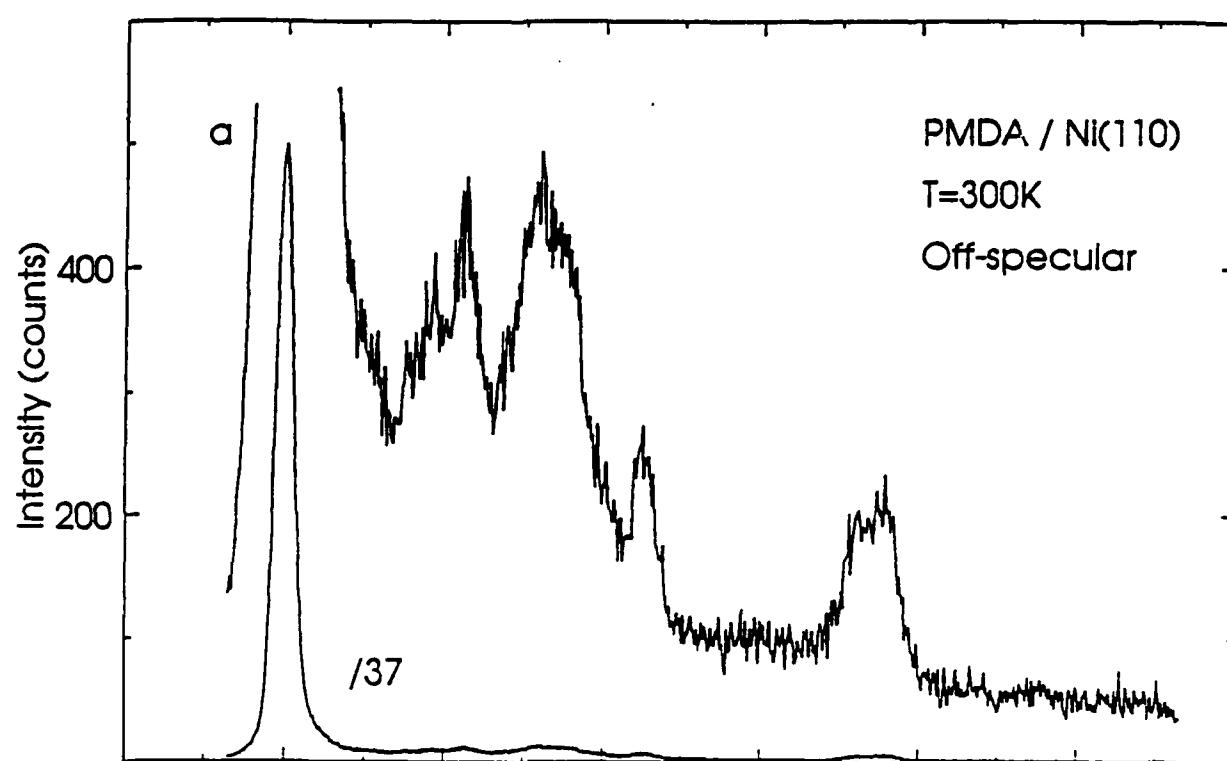
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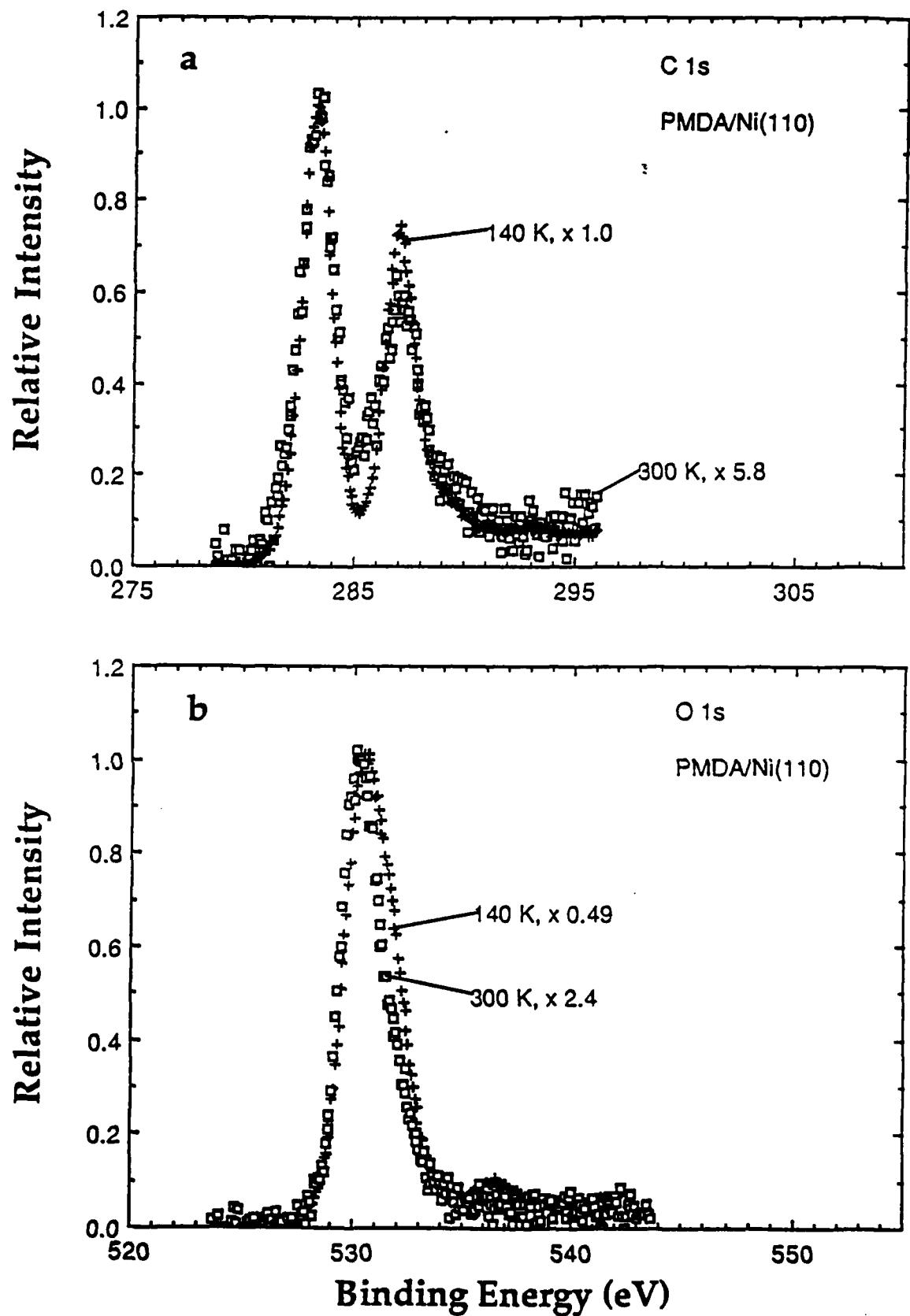


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